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(56) Documents cited
GB 1421798 A GB 1356996 A GB 1235435 A
GB 0938716 A US 4835338 A

(58) Field of search
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(54) Purification of hydrocarbons

(57) A solid particulate absorbent material, for removing acidic contaminants from hydrocarbons, comprises sodium hydroxide and/or potassium hydroxide; alumina and/or zinc oxide; lime; and, optionally, copper II oxide. A hydrocarbon containing an acidic contaminant is purified by passing the hydrocarbon through a bed of the particulate absorbent material.

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PURIFICATION PROCESS

This invention is concerned with improvements in and relating to compositions for removing acidic contaminants from hydrocarbons and to processes for purifying hydrocarbons using such compositions.

A wide variety of hydrocarbon materials, both liquid and gaseous, are treated to remove unwanted acidic contaminants. Thus, for example, olefins (such as ethylene and propylene) are purified (e.g. to remove hydrogen sulphide, carbonyl sulphide, carbon dioxide and/or sulphur dioxide) prior to catalysis to avoid poisoning or otherwise adversely affecting the catalyst employed; and liquefied petroleum gas (LPG) is treated to remove contaminants such as hydrogen sulphide and low molecular weight mercaptans. Other hydrocarbons which may be treated include gas condensates and halogenated hydrocarbons, which may be treated to remove traces of hydrogen chloride and phosgene.

The bulk removal of acidic contaminants from hydrocarbons is commonly effected by washing the hydrocarbons with caustic solutions or amines. However,

in order to obtain very low levels of contaminant (e.g. of the order of parts per billion) it is necessary to purify the hydrocarbon by passing it through a bed of an absorbent purifying material. It is an object of the present invention to provide an improved material for use in such a purification process.

According to one embodiment of the invention there is provided a solid absorbent material, for removing acidic contaminants from hydrocarbons, which absorbent material comprises sodium hydroxide and/or potassium hydroxide (especially the former); alumina and/or zinc oxide (especially the former); and lime (calcium hydroxide).

The composition also preferably contains copper II oxide; especially when the composition is to be used in the treatment of dry (anhydrous) hydrocarbon materials.

The composition of the invention suitably contains upto 10% by weight of sodium hydroxide and/or potassium hydroxide; upto 40% by weight of aluminium oxide and/or zinc oxide; from 40 to 97% by weight of lime; and from upto 40% by weight of copper oxide (when present). Preferred compositional ranges for the above components are set out in the following Table.

Table

Component	Preferred range of content (wt.%)	Most preferred range of content (wt. %)
NaOH and/or KOH	up to 10	up to 10
Al_2O_3 and/or ZnO	up to 40	up to 5 (Al_2O_3) 20 to 40 (ZnO)
$\text{Ca}(\text{OH})_2$	40 to 97	40 to 60
CuO	up to 20	10 to 20

It has been found that the water content of the composition of the invention is of importance and thus the composition suitably contains from 2 to 5% by weight of water.

The compositions in accordance with the invention may simply be formed by making a mixture of the various components together with sufficient water to form a plastic dough and subsequently forming the dough into

particulate form and drying it. In accordance with a preferred form of the invention, the dough is extruded into rods (e.g. of a diameter of 0.5 to 5 mm), and these are later broken up (after drying) into pieces of a length of 0.5 to 10 mm.

The invention also provides a method of treating a hydrocarbon material, to remove acidic contaminants therefrom, by passing the hydrocarbon through a bed formed of particulate material in accordance with the invention. In accordance with conventional practice, an installation for treating hydrocarbon materials in accordance with the invention may suitably comprise two packed beds, the material to be treated being passed through the first bed (bed A), and then the second bed (bed B), in series. When the first bed has become exhausted or absorbed contaminant to its practical limit (as judged, for example, by the amount of contaminant present in the material issuing from the bed) the bed may then be recharged with fresh material whilst the material to be treated is passed through the second bed (bed B) only. When the first bed has been replaced, the material to be treated is then passed, sequentially, through the original second bed (bed B) and thence to the original first bed (bed A) until the original second bed (bed B) has become exhausted, after which bed B is replenished and the cycle of operations recommenced.

In order that the invention may be well understood the following Examples are given by way of illustration only.

Examples 1-5

Absorbent materials having the compositions listed in Table 2 below were prepared by mixing sodium hydroxide liquid and the other (solid constituents to give a still paste. The paste was extruded, dried and granulated after which particles between 1 and 3.3 mm were separated, after which their moisture content was adjusted to 3% by weight.

Table 2
(Dry Basis)

	Sodium hydroxide (g)	Calcium hydroxide (g)	Alumina (g)	Zinc oxide (g)	Copper(II) oxide (g)
Example 1	111	1000	0	0	0
Example 2	37	1000	183	0	0
Example 3	200	1000	300	500	0
Example 4	232	1000	349	512	232
Example 5	239	1000	0	762	381

By way of comparison the following commercially available products were also tested:-

Sodalime,

Activated alumina

Both these products were crushed and separated to the same particle size as those of examples 1 to 5.

The sample materials were tested under simulated use conditions. A nitrogen gas with not more than 60 ppmv water and of known carbonyl sulphide (COS) concentration was passed upwards through a 3mm diameter, 120mm high sample bed at a GHSV of 700. The concentration of COS in the exit gas was monitored by a gas chromatographic technique. The breakthrough times equivalent to 90% and 50% removal efficiency were noted. The results are summarised in table 3.

Table 3

(Breakthrough times for products of example 1 to 5, soda lime and activated aluminium)

	Inlet COS (ppmv)	Breakthrough times	
		90% efficiency (hours)	50% efficiency (hours)
Example 1	900	3.0	4.0
Example 2	1300	4.5	5.7
Example 3	1000	2.0	4.1
Example 4	980	1.8	3.7
Example 5	1038	8.7	13.6
Sodalime	1300	4.0	5.0
Activated alumina	1370	2.7	3.3

The product of Example 5 was further tested under simulated use conditions. This time a nitrogen gas with a moisture level equivalent to 50% of its saturation capacity and of known carbonyl sulphide (COS) concentration was passed upwards through a 3mm diameter, 120mm high sample bed at a GHSV of 700. The concentration of COS in the exit gas was again monitored by a gas chromatographic technique. The breakthrough times equivalent to 90% and 50% removal efficiency were noted.

Table 4

(Breakthrough time at 50% saturation)

Inlet COS (ppmv)	Breakthrough times	
	90% efficiency (hours)	50% efficiency (hours)
1179	16	24

CLAIMS:

1. A solid particulate absorbent material, for removing acidic contaminants from hydrocarbons, which absorbent material comprises sodium hydroxide and/or potassium hydroxide; alumina and/or zinc oxide; and lime.
2. An absorbent material as claimed in claim 1 comprising sodium hydroxide, alumina and lime.
3. An absorbent material as claimed in claim 1 or claim 2 also containing copper II oxide.
4. A composition as claimed in any one of the preceding claims containing up to 10% by weight of sodium hydroxide and/or potassium hydroxide; up to 40% by weight of aluminium oxide and/or zinc oxide; from 40 to 97% by weight of lime; and up to 20% by weight of copper oxide, manganese oxide and/or cobalt oxide.
5. An absorbent material as claimed in claim 1 substantially as hereinbefore described with reference to the Examples.

6. A method of removing acidic contaminants from hydrocarbons which comprises passing the hydrocarbons through a bed of an absorbent material as claimed in any one of the preceding claims.

Relevant Technical fields		Search Examiner
(i) UK CI (Edition K)	C5E (EPK), (ECP), (ECV), (ESR)	R J WALKER
(ii) Int CI (Edition 5)	C07C	
Databases (see over)		Date of Search
(i) UK Patent Office		9 SEPTEMBER 1992
(ii) ONLINE DATABASES: WPI		

Documents considered relevant following a search in respect of claims

1-6

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 1421798 (THE DOW CHEMICAL CO) - see eg page 1 line 86-page 2 line 1	1, 2, 6 3
Y		
X	GB 1356996 (BADISCHE ANILIN AND SODA-FABRIK AG) - see page 2 lines 3-50	1, 2, 6 3
Y		
Y	GB 1235435 (STAMICARBON NV) - see whole document	3
X	GB 938716 (ESSO RESEARCH AND ENGINEERING CO) - see page 1 lines 17-45	1, 2, 6 3
Y		
X	US 4835338 (LIU) - see column 4 lines 1-19	1, 2, 6 3
Y		

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).